

NCDA&CS

Solution Analysis Methods



Plant/Waste/Solution/Media Analysis

Agronomic Division

North Carolina Department of Agriculture & Consumer Services

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<http://www.ncagr.gov/agronomi/uysoln.htm>

Solution Analysis

Solution analysis is used to test the mineral parameters of surface water, well water and nutrient solutions for varied agricultural purposes such as irrigation, fertilization (nutrient solutions), livestock and poultry production, pesticide preparation, pond management and aquaculture. The NCDA&CS Agronomic Division does not perform any testing for microbial agents (e.g. pathogens, algae) or organic contaminants (e.g. pesticides, herbicides, petroleum products). The NCDA&CS Agronomic Division does not analyze concentrated liquid fertilizers.

The standard solution analysis includes measurement of: nitrate-nitrogen ($\text{NO}_3\text{-N}$), ammonium-nitrogen ($\text{NH}_4\text{-N}$), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), sodium (Na), aluminum (Al), and chloride (Cl) concentrations. Measurements of pH, soluble salts (SS or EC), and total alkalinity as well as values of hardness and sodium adsorption ratio (SAR) are reported. For irrigation and most source waters and nutrient solutions, the amount of sulfuric acid needed to adjust alkalinity is included.

Standard solution analysis for N.C. residents	\$5.00
Standard solution analysis for non-N.C. residents	\$25.00
‡Standard solution analysis for N.C. researchers	\$12.00
‡Standard solution analysis for non-N.C. researchers	\$25.00

‡ A completed NCDA&CS Research Agreement is **required prior to submission** of research samples. *Please contact Dr. Kristin Hicks at Kristin.Hicks@ncagr.gov to set up a Research Agreement.*

In addition to the standard analysis, certain tests are available by request and for an additional fee.

Additional tests available by request:

- Molybdenum (Mo) + \$2
- Heavy Metals (cadmium, nickel, lead, arsenic, chromium, and selenium) + \$20

(Note: heavy metals analysis is available only for research purposes with a valid research agreement. No exceptions.)

- Sampling instructions: <http://www.ncagr.gov/agronomi/pdf/samsoln.pdf>
- Sample submission form: http://www.ncagr.gov/agronomi/pdf/Solution_Sample_Submission_Form_Fillable.pdf

Minimum Sample Volume

In order to obtain a representative sample, NCDA&CS strongly recommends a sample volume of 12-16 oz (~500 mL). Where this is not possible, please note the minimum sample volume required to perform each analysis (Table 1).

Table 1. Solution Methods Summary

Sample Test	Test Volume Used	Analytical Method	Reference
NO ₃ -N, NH ₄ -N, Cl ⁻	15 mL	Filtered; Continuous Flow Analysis	EPA 350.1; EPA 353.1; EPA 325.2
P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, B, Na, Al, Mo, As, Cd, Cr, Ni, Pb, Se	15 mL	Filtered; ICP-OES	EPA 200.7
pH	10 mL	As received; pH meter	AOAC 973.41
EC/SS		As received; EC meter	EPA 120.1
Alkalinity (CO ₃ and HCO ₃)	25 mL	Acid titration for total alkalinity determination	AOAC 920.194

Analytical Methods

Sample Processing & Storage

Samples are analyzed as received for pH, EC and alkalinity and filtered through a pre-folded Whatman #2 filter paper for elemental and ion analysis. Prior to analysis, samples are homogenized by shaking. Except during analysis, samples are refrigerated at 4°C.

Inorganic Nitrogen

Nitrate-nitrogen (NO₃-N) and ammonium-nitrogen (NH₄-N) are determined on a 15 mL sample which is shaken and then filtered through a pre-folded Whatman #2 filter paper (Texas Scientific Products, Argyle, TX).

NO₃-N is determined by the hydrazine reduction method, where nitrate is reduced to nitrite with hydrazinium sulfate catalyzed by Cu²⁺, under alkaline conditions and at elevated temperature (Kempers and Luft 1988). The NO₂-N concentration (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with α-naphthyl-ethylenediamine dihydrochloride to form a highly-colored azo dye which is measured at 540 nm (modified Griess reaction). (USEPA 1978b; Kempers and Luft 1988; Skalar Analytical 2018c).

NH₄-N is based on the modified Berthelot reaction where, after oxidation and oxidative coupling, a green-colored complex is formed, which is then measured at 660 nm (Krom 1980; Skalar Analytical 2018a; USEPA 1993). Both NO₃-N and NH₄-N are quantified by continuous flow analysis using an auto-flow spectrophotometric analyzer (San++ Segmented Flow Auto-Analyzer, Skalar Instruments; Breda, The Netherlands). Nitrate-nitrogen (NO₃-N) and nitrite-nitrogen (NO₂-N) are reported as NO₃-N on the Solution Analysis Report. Ammonium-nitrogen (NH₃-N + NH₄-N) is reported as NH₄-N on the Solution Analysis Report. Results are expressed in parts per million (ppm) [equivalent to mg L⁻¹].

Inorganic Nitrogen Quality Controls

Method detection limits (MDL) are determined when a new instrument or method is put into use and verified annually. **The MDLs for NH₄ and NO₃ are 0.87 ppm and 0.45 ppm, respectively.**

Samples are quantified using either a 4 or 6 point calibration curve. A method blank and duplicate spike sample are analyzed with each batch. A calibration verification solution and calibration blank are analyzed at the beginning and end of each batch and after every 10 samples. Four independent calibration verification solutions are analyzed at the beginning and end of each run. Drift checks are analyzed at the beginning and end of each run and every 20 samples. Two nitrite checks (NO₂-N) are analyzed to verify the completeness of the nitrate reduction reaction at the beginning and end of each run.

Phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), sodium (Na), aluminum (Al), molybdenum (Mo), cadmium (Cd), nickel (Ni), lead (Pb), arsenic (As), chromium (Cr), and selenium (Se)

Total elemental concentrations are determined on a 15 mL sample, which is first shaken and then filtered through a pre-folded Whatman #2 filter (Texas Scientific Products, Argyle, TX), using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Spectro Arcos EOP and Arcos II EOP, Spectro Analytical: A Division of Ametek; Mahwah, NJ) (USEPA 2001). Elements are measured at the wavelengths listed in Table 2. Results are expressed in parts per million (ppm) [equivalent to mg L⁻¹].

ICP-OES Quality Controls

Elements are measured using a calibration curve with a minimum of 5 calibration standards. A method blank, calibration blank and reference material are analyzed with each batch. A calibration verification solution is run after the daily calibration, after every 10th sample and at the end of each run. An independent calibration verification solution is analyzed at the beginning and end of each run. The method detection limits (MDLs) for each analyte are listed in Table 3.

Table 2. Wavelengths used to quantify total elemental concentrations in solutions.

Element	Wavelength (nm)
Aluminum (Al)	396.152
Arsenic (As)	189.042
Boron (B)	208.959
Cadmium (Cd)	214.438
Calcium (Ca)	183.801, 315.887, 318.128
Chromium (Cr)	267.716, 357.869
Copper (Cu)	324.754
Iron (Fe)	259.941
Lead (Pb)	220.353, 405.778
Magnesium (Mg)	279.079
Manganese (Mn)	257.611
Molybdenum (Mo)	202.095
Nickel (Ni)	341.476
Phosphorus (P)	178.287
Potassium (K)	404.721, 766.491
Selenium (Se)	196.090
Sodium (Na)	330.237, 589.592
Sulfur (S)	182.034
Zinc (Zn)	213.856

Table 3. MDLs of total elemental concentrations in solutions.

Element	MDL (ppm)
Aluminum (Al)	0.025
Arsenic (As)	0.003
Boron (B)	0.025
Cadmium (Cd)	0.002
Calcium (Ca)	2.362
Chromium (Cr)	0.004
Copper (Cu)	0.006
Iron (Fe)	0.047
Lead (Pb)	0.006
Magnesium (Mg)	1.059
Manganese (Mn)	0.003
Molybdenum (Mo)	0.001
Nickel (Ni)	0.004
Phosphorus (P)	0.022
Potassium (K)	0.193
Selenium (Se)	0.004
Sodium (Na)	0.657
Sulfur (S)	0.048
Zinc (Zn)	0.010

Chloride (Cl⁻)

Chloride concentration is determined on a 15 mL sample which is shaken and then filtered through a pre-folded Whatman #2 filter paper (Texas Scientific Products, Argyle, TX).

Cl⁻ is determined by the thiocyanate displacement method where thiocyanate is liberated from mercury(II) thiocyanate by the formation of soluble mercuric chloride. The liberated thiocyanate forms a red colored complex with ferric iron ions also present in solution (USEPA 1978a; Zall et al. 1956; Skalar 2018b). This complex is measured at 470 nm on a segmented flow analyzer (San++ Segmented Flow Auto-Analyzer, Skalar Instruments; Breda, The Netherlands). Results are expressed in parts per million (ppm) [equivalent to mg L⁻¹].

Cl Quality Control

Reference inorganic nitrogen quality control. **The MDL for Cl is 1.27 ppm.**

pH

The pH of water and solution samples is determined directly on samples at 25°C using a Thermo Scientific Orion Versa Star Pro pH meter with a Green epoxy non-fillable pH electrode with BNC connection (APHA 2012; AOAC 1990c). pH is a measure of acidity or alkalinity on a scale of 1 to 14 and is reported on this scale (unitless).

pH Quality Control

A three-buffer calibration is performed daily with a slope maintained between 98% and 102%. A duplicate solution sample is analyzed daily as a quality control sample with an acceptance criteria of ±0.2 pH units.

Electrical conductivity (EC)

Electrical conductivity (EC) is a measure of the ability of an aqueous solution to carry a current. The EC of an aqueous solution depends on the total concentration, mobility, and valence of ions and on the temperature of the sample. EC is measured directly on samples at 25°C. EC is measured using a conductivity meter and probe (SevenMulti; Mettler-Toledo, LLC; Columbus, OH) (AOAC 1990b; USEPA 1982). EC is also referred to as soluble salts (SS). EC is expressed in units of mS/cm and SS is expressed in units of 10⁻⁵ S/cm.

Electrical conductivity Quality Control

The EC meter is calibrated daily with a 1000 µS conductivity standard. A duplicate solution sample is analyzed daily as a quality control sample with an acceptance criteria of < 2% relative standard deviation.

Carbonate (CO₃) and bicarbonate (HCO₃), i.e. Total Alkalinity (AOAC 920.194)

Alkalinity is a measure of water's ability to resist change in pH (aka pH buffering capacity) and is the sum of carbonate (CO₃) and bicarbonate (HCO₃) ions in solution. Carbonate (CO₃) and bicarbonate (HCO₃) concentrations are measured by titrating a weak acid into water until the

water reaches a colorimetric endpoint, using phenolphthalein and methyl orange as endpoint indicators (AOAC 1990a). The amount of acid needed to lower the pH to the colorimetric endpoint is inversely related to the alkalinity of the water. CO_3 and HCO_3 are reported in meq L^{-1} . Total alkalinity (TA) is reported in ppm of calcium carbonate (CaCO_3) and is calculated as follows:

$$TA = (\text{CO}_3 + \text{HCO}_3) \times 50$$

Carbonate and Bicarbonate Quality Control

A three-buffer calibration is performed daily with a slope maintained between 98% and 102%. A duplicate solution sample is analyzed daily as a quality control sample with an acceptance criteria of <3% relative standard deviation.

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